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Corresponding Author: James Smialek, Dr.

Corresponding Author's Institution: NASA Glen Research Center

First Author: James Smialek, Dr.

Order of Authors: James Smialek, Dr.

**Abstract:** Delayed failure of TBCs is a widely observed laboratory phenomenon, although many of the early observations went unreported. "The weekend effect" or "DeskTop Spallation" (DTS) is characterized by initial survival of a TBC after accelerated laboratory thermal cycling, then failure by exposure to ambient humidity or water. Once initiated, failure can occur quite dramatically in less than a second. To this end, the water drop test and digital video recordings have become useful techniques in studies at NASA (Smialek, Zhu, Cuy), DECHMA (Rudolphi, Renusch, Schütze), and CNRS Toulouse/SNECMA (Déneux, Cadoret, Hervier, Monceau). In the present study the results for a commercial turbine blade, with a standard EB-PVD 7YSZ TBC top coat and Pt-aluminide diffusion bond coat are reported. Cut sections were intermittently oxidized at 1100°C, 1150°C, and 1200°C and monitored by weight change and visual appearance. Failures were distributed widely over a 5-100 hr time range, depending on temperature. At some opportune times, failure was captured by video recording, documenting the appearance and speed of the moisture-induced spallation process. Failure interfaces exhibited alumina scale grains, decorated with Ta-rich oxide particles, and alumina inclusions as islands and streamers.

The phenomenon is thus rooted in moisture-induced delayed spallation (MIDS) of the alumina scale formed on the bond coat. In that regard, many studies show the susceptibility of alumina scales to moisture, as long as high strain energy and a partially exposed interface exist. The latter conditions result from severe cyclic oxidation conditions, which produce a highly stressed and partially damaged scale. In one model, it has been proposed that moisture reacts with aluminum in the bond coat to release hydrogen atoms that 'embrittle' the interface. A negative synergistic effect with interfacial sulfur is also invoked.

## Moisture-Induced TBC Spallation on Turbine Blade Samples

James L. Smialek

NASA Glenn Research Center

Delayed failure of TBCs is a widely observed laboratory phenomenon, although many of the early observations went unreported. “The weekend effect” or “DeskTop Spallation” (DTS) is characterized by initial survival of a TBC after accelerated laboratory thermal cycling, then failure by exposure to ambient humidity or water. Once initiated, failure can occur quite dramatically in less than a second. To this end, the water drop test and digital video recordings have become useful techniques in studies at NASA (Smialek, Zhu, Cuy), DECHMA (Rudolphi, Renusch, Schütze), and CNRS Toulouse/SNECMA (Déneux, Cadoret, Hervier, Monceau). In the present study the results for a commercial turbine blade, with a standard EB-PVD 7YSZ TBC top coat and Pt-aluminide diffusion bond coat are reported. Cut sections were intermittently oxidized at 1100°, 1150°, and 1200°C and monitored by weight change and visual appearance. Failures were distributed widely over a 5-100 hr time range, depending on temperature. At some opportune times, failure was captured by video recording, documenting the appearance and speed of the moisture-induced spallation process. Failure interfaces exhibited alumina scale grains, decorated with Ta-rich oxide particles, and alumina inclusions as islands and streamers.

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## **1.0 Introduction and Background**

Thermal barrier coatings (TBC), widely used on metallic combustor liners and airfoils in turbine engines, may suffer degradation from surface sintering, phase transformations, CMAS and salt deposits, cyclic damage, and bond coat oxidation and rumpling, to name a few. Regarding bond coat oxidation, it is well established that the integrity of a thin, adherent, slow-growing alumina scale at the TBC-bond coat interface is required for optimum performance. Specifically, any factor that encourages scale spallation may ultimately trigger debonding and failure of the TBC. Accordingly, beneficial noble metal, reactive element, and detrimental sulfur impurity effects on scale growth and adhesion to the bond coat become of paramount importance.

In addition, moisture has often been found to be a negative factor in laboratory tests regarding alumina scale adhesion and TBC failure. That is, scales and TBCs that were otherwise adherent in normal furnace cycling were found to fail when exposed to ambient moisture contents, well after cool down to room temperature. This is not to say that young adherent alumina scales are subject to moisture effects. Indeed, the detrimental effects only arise for at risk or mature scales. There is a continuum of degradation factors that come in play for the effect to be manifested: moisture effects become more pronounced as the scales are subjected to greater strain energy and cyclic damage, i.e., mature (thick) scales that have some cracking or spalling. Simple diffusion aluminide bond coats do not have optimum scale adhesion and are subject to the detrimental effects of sulfur interfacial segregation and voiding. The above factors increase the probability of some interfacial spalling and access of ambient humidity to exposed metal. It is this situation that is ripe for Moisture-Induced Delayed Spallation (MIDS).

Indeed a ‘sweet zone’ for MIDS can be conceptually described at a given level of adhesion. It is determined by sulfur and/or Pt, Y, Hf, etc. dopant content and broadens with moisture level, time of exposure, strain energy, and cyclic damage, **Figure 1**. In **Figure 1a**, the amount of retained scale after cool down is shown schematically as a sigmoidal curve, increasing as sulfur content decreases from critical contents of about 1 down to 0.1 ppmw. The amount of retained scale after moisture exposure is shown as another sigmoidal curve, but below that of the as-cooled curve. Thus the observed moisture effect is the difference between the two, **Figure 1b**, and is a maximum at some intermediate sulfur (or Pt, Y, Hf) level. At higher sulfur levels, the scale spalls initially on cooldown before any moisture exposure, at lower levels the scale remains

adherent even after moisture exposure. The shiftable nature of the ‘sweet zone’ accounts for the rather enigmatic nature of the phenomenon. These characteristics and an extensive defense of a possible mechanism were presented in a recent position paper [1]. Here it was postulated that moisture can react with aluminum in the bond coat to form an hydroxide molecule, releasing hydrogen into the strained interface and degrading adhesion. A number of tangential observations are presented in defense of this hypothesis. Indeed, supporting cathodic hydrogen charging experiments were shown to produce interfacial alumina scale spallation for mature cycled scales on Rene $\square$  N5+Y[2,3].

Regarding TBC phenomena more specifically, an early indication of a moisture effect was the observation of slow delamination (blister) growth in a PVD TBC as detected by photoluminescence (piezospectroscopy) of the underlying alumina scale [4]. Studies of oxidized APS TBCs on no-bond coat superalloys were found to completely detach unexpectedly, well after cool down, but especially upon water immersion in 1100° and 1150°C tests [5, 6]. Video recordings were later used to demonstrate water drop induced spallation of a PVD TBC from a Pt-aluminide bond coat after 300 hr cyclic oxidation at 1150°C [7]. The water drop video test, combined with acoustic emission, revealed the cracking history and PVD TBC delamination from a VPS NiCoCrAlY bond coat that was oxidized isothermally for 310 hr at 1050°C [8,9]. In addition, PVD TBCs on Pt-aluminide bond coats could survive 200 1-hr cycles at 1150°C when stored in dry atmospheres indefinitely, but failed above 170 hr when exposed to ambient humidity or water [10]. Many of these studies show that moisture encourages TBC spallation by decreasing adhesion of the alumina scale to the metal bond coat. That is to say, DTS and MIDS are rooted in the same sensitivity of the oxide metal interface to moisture.

While confirmed in the laboratory, the same moisture phenomenon has not been observed in the field or in service. Component and engine design avoid severe bond coat oxidation and preclude the high strain energy needed to sensitize the interface to hydrogen or whatever the root cause may be. Given this background, the purpose of the present study was to demonstrate, by accelerated laboratory exposures, the water test on coated commercial hardware samples. These were sectioned from an actual engine blade pulled from service. Failure modes were noted at various intervals for 1100°, 1150°, and 1200°C intermittent oxidation tests. On occasion, the spalling event was able to be captured on video. The resulting failure surfaces are characterized

by optical and SEM (scanning electron microscopy) techniques, including backscatter electron (BSE) imaging and energy dispersive spectroscopy (EDS).

## **2.0 Experimental**

First stage turbine blades were obtained from a prominent company. They had been removed from service in an aero-derivative ground power installation. The blade was a directionally solidified Ni-base superalloy. The TBC was an EB-PVD 7YSZ TBC using a commercial Ni(Pt)Al chemically vapor deposited (CVD) platinum aluminide diffusion coating. One blade was sectioned into three ~ 1 cm high chord slices (#A, B, C) which were then sectioned into six ~ 1 cm wide specimens (#1, 2, 3, 4, 5, 6). All specimens had cut edges polished with SiC emery to a 600 grit finish. The samples were ultrasonically cleaned in detergent, then in alcohol and dried. Examples of the sliced specimens, chords B and C, are shown in [Figure 2](#). The sectioned samples are labeled 1 through 6 starting at the leading edge as shown. Some sections (#1,5,6) present larger amounts of TBC coated surface on both pressure (concave) and suction (convex) sides. Others have essentially one major TBC surface due to the blade curvature. It can be seen that the samples present many internal uncoated surfaces as well as the cut edges. Both of these issues will complicate the interpretation of oxidative weight changes, especially at higher temperatures. Also, weight changes are reported in terms of mg and not mg/cm<sup>2</sup> for the same reasons.

The specimens from each chord section were oxidized intermittently at 1100°, 1150° and 1200°C for the slices named A, B, and C, respectively. The samples were placed in a high purity alumina boat and inserted/retracted manually in a box furnace. Various heating durations were used, generally following the progressive schedule of 1, 2, 5, 10, 15, ...50, 75, 100 hr, total time. Samples were weighed to  $\pm 0.05$  mg after each cooldown until failure, generally occurring under 50 hr, depending on the test temperature and sample. The weights were corrected for any balance drift by frequently weighing the same calibrated 3.00000 g standard weight. For some exposures, the samples were subjected to sequential immersions in acetone, alcohol, and water in order to isolate any effects of water from other liquids. As indications of failure became evident, one or more of the duplicate samples were exposed to a water drop and often monitored by digital video recording. Final weights of rinsed and dried samples were again recorded to detect

any coating spallation. Failed interfaces of the blade and collected TBC fragments were examined by SEM/EDS.

### **3.0 Results**

Prior to oxidation, an as-received blade was exposed to water immersion and exhibited no effect. Attempts to debond by cathodic hydrogen charging also exhibited no effect. The moisture effect was only produced by subjecting the samples to accelerated oxidation (below), with partially exposed scale-metal interfaces.

#### **3.1 1100°**

The weight change with 1100°C oxidation time is shown for chord A samples in **figure 3**. Here the test begins with most samples producing a small weight gain on the order of 1 mg in the first 10 hr. Eventually, weight loss occurred at an average rate (dashed line) of about 0.15 mg/hr after 10 hr, just due to oxidative issues with the cut surfaces of the blade alloy. Additional drops in weight, often quite abrupt, occurred with partial TBC coating loss on one major surface of a sample. Failure occurred by both normal cool down stresses or by the water drop test, randomly, depending on the sample. (The water drop failures are indicated by the star-point symbols). Sample A1 exhibited a small amount of bare metal spallation at the leading edge after cool down from 40 hr of oxidation. Sequential immersions in acetone, alcohol, and water were performed at the 10, 15, and 40 hr test times, producing little additional weight loss. Sample A2 exhibited partial delamination early in the test, but the TBC remained loosely attached. It was subjected to the same sequential immersions as A1, again with little effect. Some loose TBC segments chipped off at 20 and 40 hr just due to handling. Sample A3 lost one surface of the TBC due to water immersion after just 10 hr of oxidation. Samples A4, A5, and A6 were relatively unaffected for the first 50 hr. Thus moisture induced failures can be seen for sample A3, A2, A1, and A5 occurring at 10, 45, 75, and 100 hr. total oxidation time, respectively. Failure by natural cooling also occurred for the other side of sample A1 at 75 hr.

It is also important to acknowledge when failure does not occur by water drop testing and how these times relate to cooling failures, if any. It goes without saying that any moisture induced failure implies that the coating survived cooldown. Accordingly, a summary of the failure history of each sample is presented in **Figure 4**. Here it can be seen that sample A1 first

exhibited cooling spallation at 75 hr, with more gradual losses from subsequent water exposures. Sample A2 survived moisture testing at 40 hr., then failed on immersion at 45 hr. and was pulled from further testing. Sample A3 survived immersion at 5 hr, then failed at just 10 hr, and this sample was also pulled. Sample A5 survived the water drop test at 50 and 75 hr, then failed with a water drop on one side at 100 hr. Finally, samples A4 and A6 both survived cooldown up to 100 hr oxidation (no water test yet), and are still in test.

### 3.2 1150°

The weight change response for testing chord B at 1150°C is shown in [figure 5](#). Here about 10 mg weight loss was occurring after 20 hr just due to blade alloy oxidation, or at an average rate of 0.5 mg/hr. An additional 50 mg or so drop in weight, often quite abrupt, was generally associated with coating failure on one major surface of a sample. Moisture induced failures can be seen for samples 1-4, occurring over 12.5 to 35 hr total test time. A summary of the survival/failure history of each sample is presented in [figure 6](#). Here it can be seen that sample B1 first exhibited cooling spallation and subsequent water failure occurring at 12.5 hr. Sample B2 survived moisture testing at 10 hr, then failed at 15 hr. Sample B3 showed partial failure on cooldown and more with moisture exposure after 15 hr, then completed spallation by moisture failure at 16 hr. Sample B4 survived the water drop test at 20 hr, then partially failed at 22.5 hr. The remnant coating survived moisture exposure at 30 hr, then failed at 35 hr. Finally, samples B5 and B6 both survived cooldown and the water drop test at 20 hr, then failed on cooldown at 40 hr (due to the final long 20 hr interval with no inspection interval inbetween).

### 3.3 1200°C

The weight change response for testing chord C at 1200°C is shown in [figure 7](#). Now the oxidation of the base metal produced nearly 50 mg weight loss after just 5-10 hr oxidation, or at an average rate of ~7 mg/hr. These large losses obscured any additional abrupt drops in weight associated with visual observation of coating failure. Moisture induced TBC failures are noted for samples C1, C2, C4, and C6 occurring at 5, 10, 15, and 20 hr total test time. A summary of the survival/failure history is presented in [figure 8](#). Here it can be seen that sample C1 spalled exclusively by water failure at just 5 hr. Sample C2 spalled partially by cooldown, then by moisture testing, both at 10 hr. Samples C3-C6 exhibited partial failure on cooldown from 10-20

hr, survived moisture testing for 5-15 hr, and failed in water drop tests at 15 and 20 hr. At this temperature the overlap of the various survival/failure times were more prevalent, as the lifetimes become highly compressed due to greater degradation and oxidative stresses.

### 3.4 Optical macro, microphotos of visual appearance and video recording of spallation.

The appearance of a cut surface of sample B2, oxidized at 1150°C for 5 hr is shown in the macrograph of [Figure 9](#). The TBC is seen to be intact as the white top layer. It is attached to the Ni(Pt)Al bond coat which exhibits only modest oxidation. The exposed substrate however shows a preponderance of blue (NiAl<sub>2</sub>O<sub>4</sub> spinel) scale. Spalling to bare metal (reflective) and large grain NiO nodules (dark) can be seen in local areas (arrows). These substrate features undoubtedly account for the majority of the weight changes discussed above that were not associated with TBC spallation.

The water test sometimes results in complete delamination and removal of the TBC in large intact pieces. Such a result is shown in [Figure 10](#) for sample C2 that failed by immersion in water for 2 min. after 5 hr oxidation at 1200°C. The single TBC flake is positioned against the surface it delaminated from, but flipped inside out for an improved view. The metal side revealed after delamination is seen to be relatively clean and oxide-free.

F3.4-3. A3, 1100°C, 10 hr, 10x. Exposed metal of bond coat and retained TBC.

Another typical appearance of a tested and failed sample is shown in [Figure 11](#). Here some TBC is shown damaged and detached or partially adherent. The exposed bond coat is also apparent as reflective clean metal. Bond coat damaged from chipping, then producing substrate oxidation, is seen around the cut edges.

Often, the TBC was observed to delaminate in very small fragments in a more or less sequential fashion, progressing from a single failure point, generally near a cut edge. A video sequence of such a progression was obtained for a number of samples when they were exposed to a water drop stream from a wash bottle. Still frames captured from such a video are presented in [Figure 12](#) for sample C6 oxidized at 1200°C for 15 hr. The first frame shows the intact sample as the water stream is applied from the upper right. The superimposed time code bar is in hr:min:sec; 1/30 sec., indexed from the start of the video. The next frame shows that failure initiated at the

upper right edge (arrow) after about 22 seconds of water exposure. Then the rapid progression of delamination is seen in the subsequent frames, spanning about 1 sec. additional cumulative time expired. In the lower left frame both water and a TBC segment (arrows) are captured in flight due to the energetic detachment of the TBC. The water droplet can then be found in the bottom center frame at rest on the table top (arrow). After rinsing and drying (not shown), very little TBC remained bonded to the sample.

Of the five videos obtained, the time interval between the application of moisture and the first sign of TBC spallation ranged from 1 second to nearly 3 minutes, **Table 1**. However the interval for spallation to be completed ranged from only 1 to 7 seconds. Indeed the spallation events appeared instantaneous in many regards. The longer intervals were associated with partial spalling and additional incubation time before the next spallation event for the adjacent coating. The sequence of spallation in each video was similar in that failure would start at one edge or corner and progress across the sample. There was no apparent correlation of either of these times with oxidation temperature or time.

While the overall exposed bond coat appearance is that of clean reflective metal, closer examination reveals additional detail. **Figure 13** is an optical surface micrograph of sample C2, oxidized at 1200°C for 5 hr. before failing by water immersion. It shows a series of entrained scale in more or less a grid like network of stringers.

### 3.5 SEM analysis of failed interfaces.

The surfaces exposed by TBC delamination were examined by SEM/EDS. **Figure 14** shows a typical area of the underside of a spalled fragment of coating. For the most part, the TBC fragment retained the thermally grown alumina scale which exhibited an undulating or rumpled morphology (**1a**). The scale underside grain morphology is apparent (**1b**) with most grains being in a 1-2  $\mu\text{m}$  range. Some highlighted areas in backscatter imaging were shown by EDS to be Ni,Ta- rich oxide or Ni metal alloy. Attempts were made to examine the attached alumina scale in fracture sections of spalled TBC fragments, **Figure 15**. Unfortunately, no good section views of the scale were found, even though EDS identified the alumina scale away from the fracture section. It is seen that the TBC layer was about 140  $\mu\text{m}$  thick here.

At the exposed side of the blade, much bare metal was revealed with an array of included alumina stringers, **Figure 16**, spaced about 0.2 - 0.5 mm. These stringers are seen to be somewhat wrinkled, distorted and porous, **Figure 17**, with numerous patches of bright particles found by EDS to be Ta or Zr-rich oxide. At higher magnification, the alumina stringers are seen to be highly convoluted lamellae and not dense. There are layered duplex grain morphologies indicative of multiple growth sequences, perhaps triggered by cyclic exposures, rumpling, and local detachment of the scale, but without removal by spallation. Finally, the oxide grain imprints, **Figure 18** are decorated with lower Al content lenticular precipitates, presumably an Al-depleted Ni-rich phase. Other bright areas, scattered sporadically over the bond coat surface, were noticeably Ta-rich.

#### **4.0 Discussion**

The results show that a typical TBC on a turbine blade can be made to fail by accelerated oxidation and moisture exposure. While water was used in this test, there is much precedent to show that delayed failure of alumina-metal systems exhibit delayed failure in ambient humidity. This includes the “desktop spallation” delayed failure phenomenon specific to TBCs. Significant scatter can be expected. Indeed there is an element of luck involved with capturing a video of a water drop failure, as failure may occur first on cooldown or may not occur for many more hours of testing. Be that as it may, there does appear to be a strong temperature effect on moisture induced failure, reaching 75-100 hr or more at 1100°C, 15-35 hr. at 1150°C, and 5-20 hr at 1200°C. This attests to the increase in stored strain energy in the scale from both the increase in scale thickness with temperature at a given time, as well as the increase in the delta temperature operative for CTE mismatch stresses. Of course the CTE mismatch stress is experienced even on the first cycle, so the scale thickness and progressive damage are seen as necessary factors for failure.

In that regard, it is helpful to compare these results with previous studies. A similar coating was tested on tests discs and survived 280 1-hr cycles at 1150°C before failing by water drop testing after 300 cycles [7]. Other similar coatings failed between 220 and 440 hr. In a definitive, extensive study of EB-PVD coatings on a Ni(Pt)Al bond coat, it was found that 5  $\mu\text{m}$  of alumina scale was needed to be grown before moisture effects were noted [10]. This required at least 170

cycles (15 min. heat up + 45 min. hot) to 1150°C. They further show that failure can be put off by retaining cooled specimens in low humidity, then forced by exposure to ambient humidity. Thus in general the cut blade sections in the present study appeared to fail at a small fraction of the lives of new coated test buttons. Other geometric factors may come in to play as well, as the highly curved sections labeled #1-3 generally failed before the flatter regions in sections #4-6.

Given that bare reflective metal is exposed upon the water induced failure, we can conclude again that the oxide-metal interface is the affected location. The rapidity and explosiveness of the spallation process reflects the release of high levels of stored strain energy in the scale. Incubation times may be a few seconds to a few minutes, but generally the delamination process is complete in the interval of 1-2 seconds. These observations are similar to those reported in [7-10]. Given the working hypothesis that hydrogen embrittlement is the root cause, this feature may be problematic with diffusion times required for hydrogen to transit from one initiation site to the other side of the sample. There seems to be an autocatalytic detachment triggered as soon as new interface is exposed. This may attest to rapid chemical transitions once Al in the metal is exposed to water molecules. It may also indicate that the interface was partially compromised before the detachment front arrived. For example, moisture may have already penetrated all parts of the entire TBC and began to access the scale-metal interface through cracks in the scale.

One might also envision some aspect of adsorbed droplet surface tension to be affecting interfacial strength. Along these lines, other liquids (acetone, then 200 proof alcohol) were used prior to water immersion after a number of exposures at 1100°C. However they were never successful in initiating TBC delamination. (Only some slight weight loss resulted from removal of complex oxides from the cut edges of superalloy.)

In review, the observations in the present study are consistent with the prior studies showing moisture-induced DTS [5-10]. As proven by Deneux et al., [10] a minimum amount of pre-oxidation (i.e., scale thickness) is required to sensitize the system to moisture-induced spallation. Spallation may be delayed indefinitely if suitably pre-oxidized coatings are sequestered from moisture. Re-introduction of moisture then causes failure at various incubation times inversely related to the level of moisture (e.g., ambient vs water drop or immersion).

The atomistics of the failure process are still a matter of study and conjecture and are beyond the scope of the present study. However, we have discussed the general elements of DTS in the context of MIDS [11]. That is to say, hydrogen ‘embrittlement’ had been proposed as the mechanism fundamental to both. While interfacial hydrogen detection is a difficult task [12], the existence of subsurface cracks in the bond coat after water exposure provides indirect but very significant corroborating evidence [10]. Alternatively, hydrogen charging by cathodic polarization was sufficient to detach mature alumina scales that had already been shown to survive water immersion [2,3]. Other supporting circumstantial evidence, derived from a number of tangentially related fields, has been presented in a more detailed position paper for the purpose of discussion [1]. These points can be briefly summarized as:

- Hydrogen gas is produced by reaction of water and Al powders.
- H was detected at the scale-metal interface of anodized Al.
- *Ab initio* studies report a 90% decrease in Co - Al<sub>2</sub>O<sub>3</sub> interfacial strength due to H.
- H<sub>2</sub> gas, moist air and Ar, and electrochemical H-charging all reduce the ductility of Ni<sub>3</sub>Al, Fe<sub>3</sub>Al, FeAl, and Alloy 718 compared to dry air or vacuum.
- Cathodic H-charging of pure Ni increases the fracture area of intergranular embrittlement from 2% up to 95%, in combination with segregated sulfur.
- Exposure to moisture or H and D-implantation produce bubbles under native alumina films on Al. (He-implantation does not).

Thus the various chemical factors in play for alumina scale adhesion may now include hydrogen, in addition to sulfur and reactive elements. Though not discussed at length in the present study, previous work suggests that hydrogen may work in concert with sulfur segregation, even at low levels, in reducing scale adhesion. While the present set of experiments may not be directly related to performance in service, it does emphasize the importance of moisture to our understanding of alumina scale adhesion. This factor is usually not considered when performing normal cyclic life tests. The observed failure time may be affected by the frequency and duration of exposure to true ambient room conditions on cool down, which can be shown to have much higher relative humidity than the cooling environment in many cyclic tests. It also raises interesting conceptual questions, such as how much life extension might be gained if there were no moisture sensitivity or dependence on hydrogen.

## **5.0 Summary and Concluding Remarks**

This study has again shown that moisture may induce TBC failure at room temperature, consistent with desktop TBC spallation phenomena near their oxidative limits. It has used cut sections of a turbine blade retired from service and thus relates to actual engine hardware, but in extreme or accelerated tests. A strong temperature dependence was shown, producing water immersion or water drop failures at a maximum of 100, 35, and 20 hr for interrupted oxidation tests at 1100°C, 1150°C, and 1200°C, respectively. Sample video recordings of the failure process showed that incubation times of 1 second to 2 minutes may be needed, but then completed in a matter of seconds. The failure surface was unequivocally at the scale-metal interface. After TBC spallation, the reflective metal of the bond coat was easily observed visually and confirmed by subsequent SEM of the metal, showing imprints of the oxide grains and EDS spectra for the Ni(Pt,Ta)Al interdiffused bond coat. A network of alumina stringers in the metal was suggestive of biaxial strains, perhaps related to rumpling or craze cracking of the bond coat. The mating side of the spalled TBC was universally covered with alumina. However fracture cross sections were not immediately productive for measuring scale thickness. The results, in total, are consistent with all prior DTS studies. They suggest that moisture exposures play a role in TBC failure after cooldown because of detachment of the alumina scale from the bond coat. If these humidity/moisture exposures vary in level, frequency, or duration, they may result in corresponding variations in lifetimes as measured in laboratory tests.

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Captions

Table I. Video recorded incubation and propagation times for water drop TBC delamination after various oxidation treatments.

Figure 1. Schematic sigmoidal trend in scale retained after cooling and moisture exposure as sulfur content is reduced. a) Shift in final retained scale to lower sulfur levels due to moisture factors. b) Net amount of moisture-induced spallation is best manifested at an intermediate level of adhesion.

Figure 2. Sliced TBC coated turbine blade chord and six test sections for water drop experiments. Section C as-cut and sanded and Section B after oxidation at 1150°C for 5 hr.

Figure 3. Mass losses for 1100°C intermittent oxidation of Section A samples. Water drop spallation failures indicated by star symbol. Dashed line indicates approximate loss rate for uncoated superalloy cut edges.

Figure 4. Survival/failure history for TBC spallation from cool down and water drop tests. Section A, 1100°C intermittent oxidation. 100 hr maximum failure time for water drop (so far).

Figure 5. Mass losses for 1150°C intermittent oxidation of Section B samples. Water drop spallation failures indicated by star symbol. Dashed line indicates approximate loss rate for uncoated superalloy cut edges. Horizontal dot/dash lines indicate approximate magnitude of mass loss due to TBC spallation from 1 or both major surfaces.

Figure 6. Survival/failure history for TBC spallation from cool down and water drop tests. Section B, 1150°C intermittent oxidation. 35 hr maximum failure time for water drop.

Figure 7. Mass losses for 1200°C intermittent oxidation of Section C samples. Water drop spallation failures indicated by star symbol. Dashed line indicates approximate loss rate for uncoated superalloy cut edges.

Figure 8. Survival/failure history for TBC spallation from cool down and water drop tests. Section C, 1200°C intermittent oxidation. 20 hr maximum failure time for water drop.

Figure 9. Optical micrograph of cut edge of sample B2 after 5 hr oxidation at 1150°C. Intact TBC, lightly oxidized bond coat, dark NiO nodules and bright bare metal spalling on superalloy cut edge.

Figure 10. Optical macrograph of Sample C2 after complete TBC delamination from water drop test following 5 hr intermittent oxidation at 1200°C.

Figure 11. Optical macrograph of Sample A2 after partial TBC delamination resulting from water drop test following 10 hr intermittent oxidation at 1100°C. Reflective bare metal bond coat revealed under delaminated TBC and multiply cracked retained TBC area.

Figure 12. Selected frames of a video sequence recording the water drop test for sample C6 after 15 hr intermittent oxidation at 1200°C. 22 seconds for incubation and fractions of a second for successive delamination. Arrows show crack initiation, water droplet and coating in flight, and water drop at rest.

Figure 13. Optical macrograph of Sample C2 after TBC delamination resulting from a 2 minute water drop test following 5 hr intermittent oxidation at 1200°C. Reflective bare metal bond coat and network of retained oxide.

Figure 14. Backscatter SEM image and EDS spectra of exposed alumina grain surfaces attached to the underside of the spalled TBC. Sample B4, 35 hr intermittent oxidation at 1150°C.

Figure 15. Backscatter SEM image of a fracture edge of the spalled TBC. Sample B4, 35 hr intermittent oxidation at 1150°C.

Figure 16. Backscatter SEM image of the exposed metal surface showing a network of entrained alumina scale stringers. Sample B4, 35 hr intermittent oxidation at 1150°C.

Figure 17. Higher magnification backscatter SEM image of the entrained alumina from Figure 16 showing separated lamellae and duplex grain structures. Sample B4, 35 hr intermittent oxidation at 1150°C.

Figure 18. Backscatter SEM image of the exposed metal surface (and corresponding EDS) showing alumina scale grain imprints, with boundaries decorated by Ni-rich lenticular particles. Sample B4, 35 hr intermittent oxidation at 1150°C.

# Water Drop TBC Failure Times from Video

(7YSZ on Ni(Pt)Al on Blade Sections)

sample	oxidation		spallation (seconds)	
	temperature	hours	incubation	propogation
B1	1150°C	12.5	1	2
B4		30	163	1
C1	1200°C	10	3	5
C6-a		15	22	2
C6-b		20	4	7

# Schematic of Moisture Effect

(residual scale after cooling, then moisture damage)

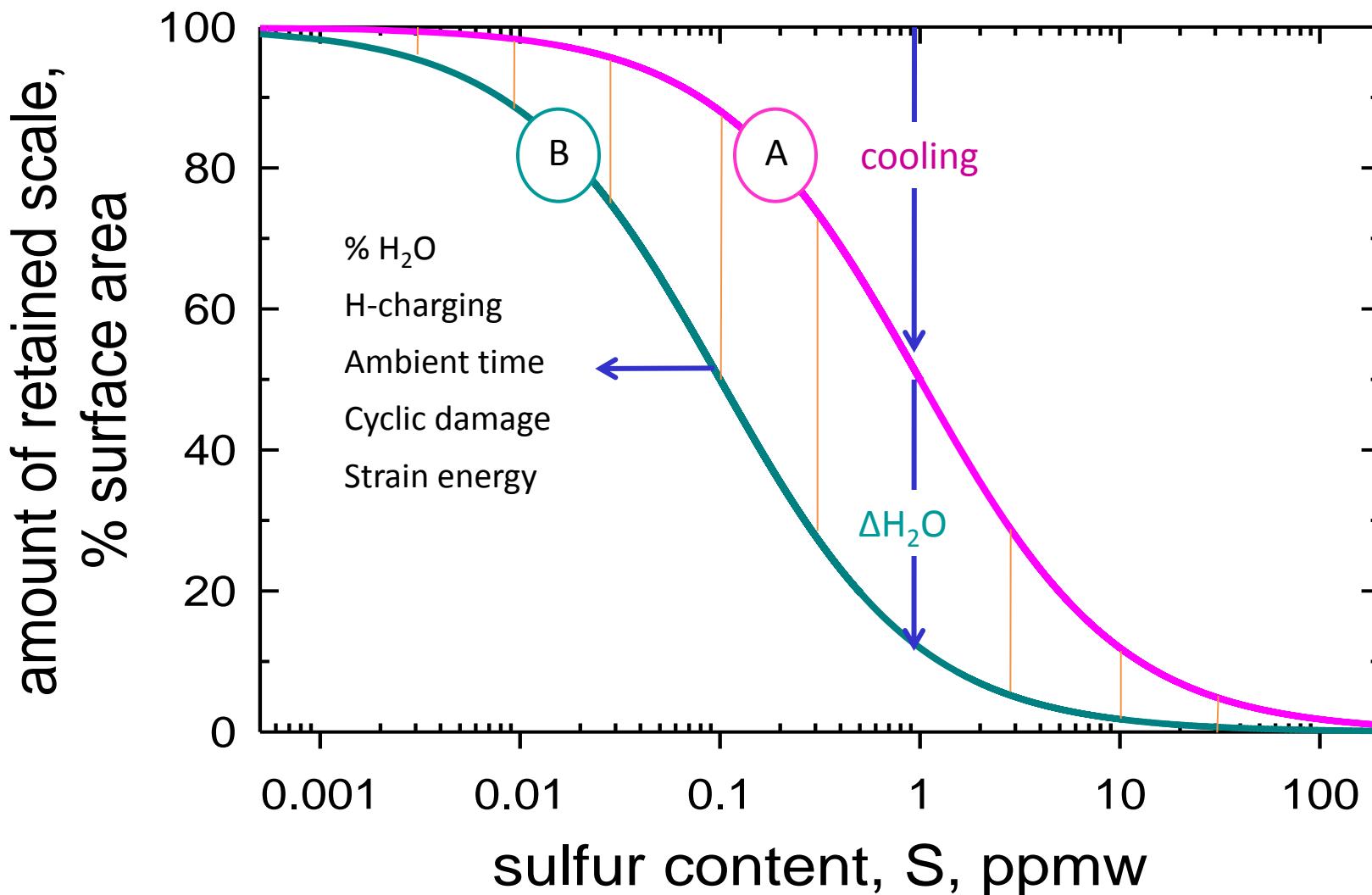


Figure 1a

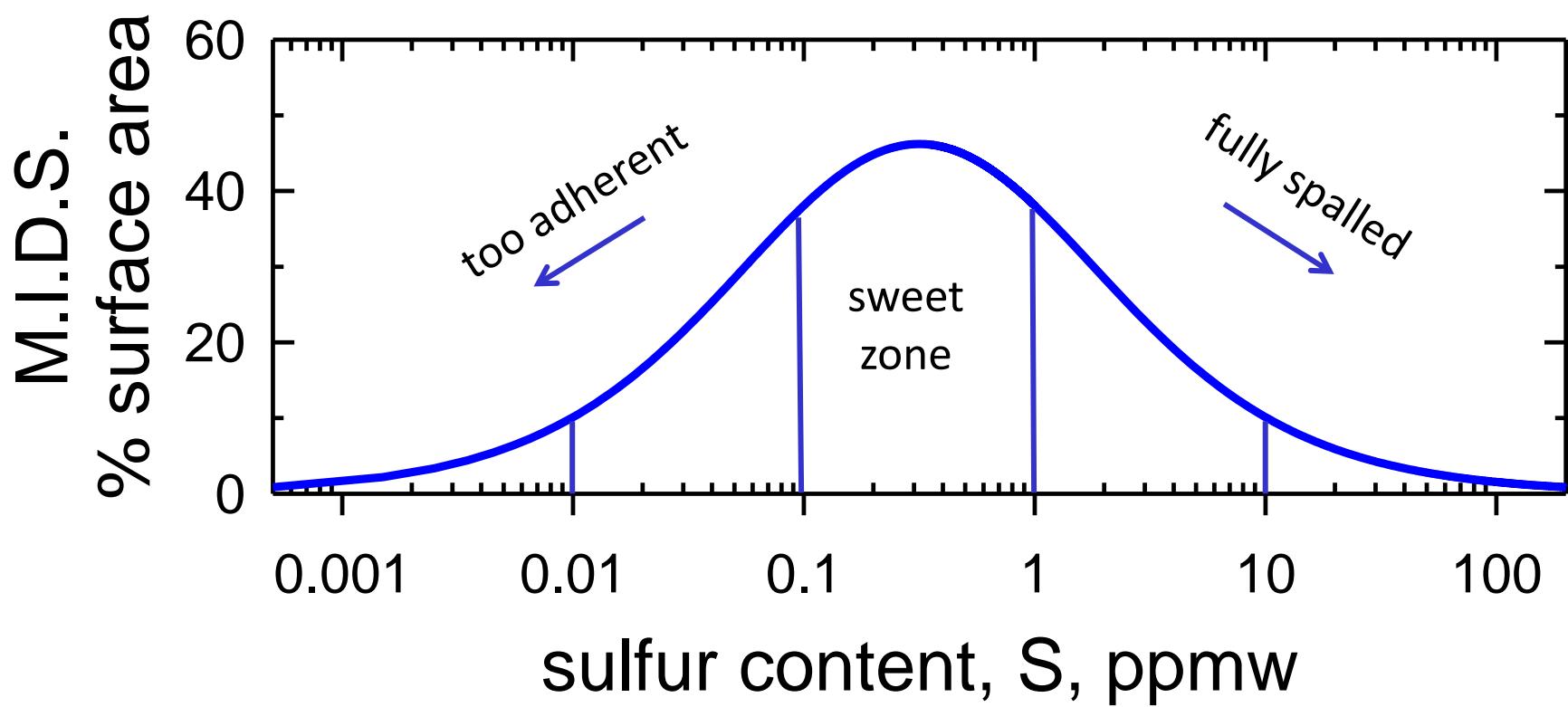


Figure 1b

# EB PVD YSZ, Pt-Al, Sliced HPT Blade Sections

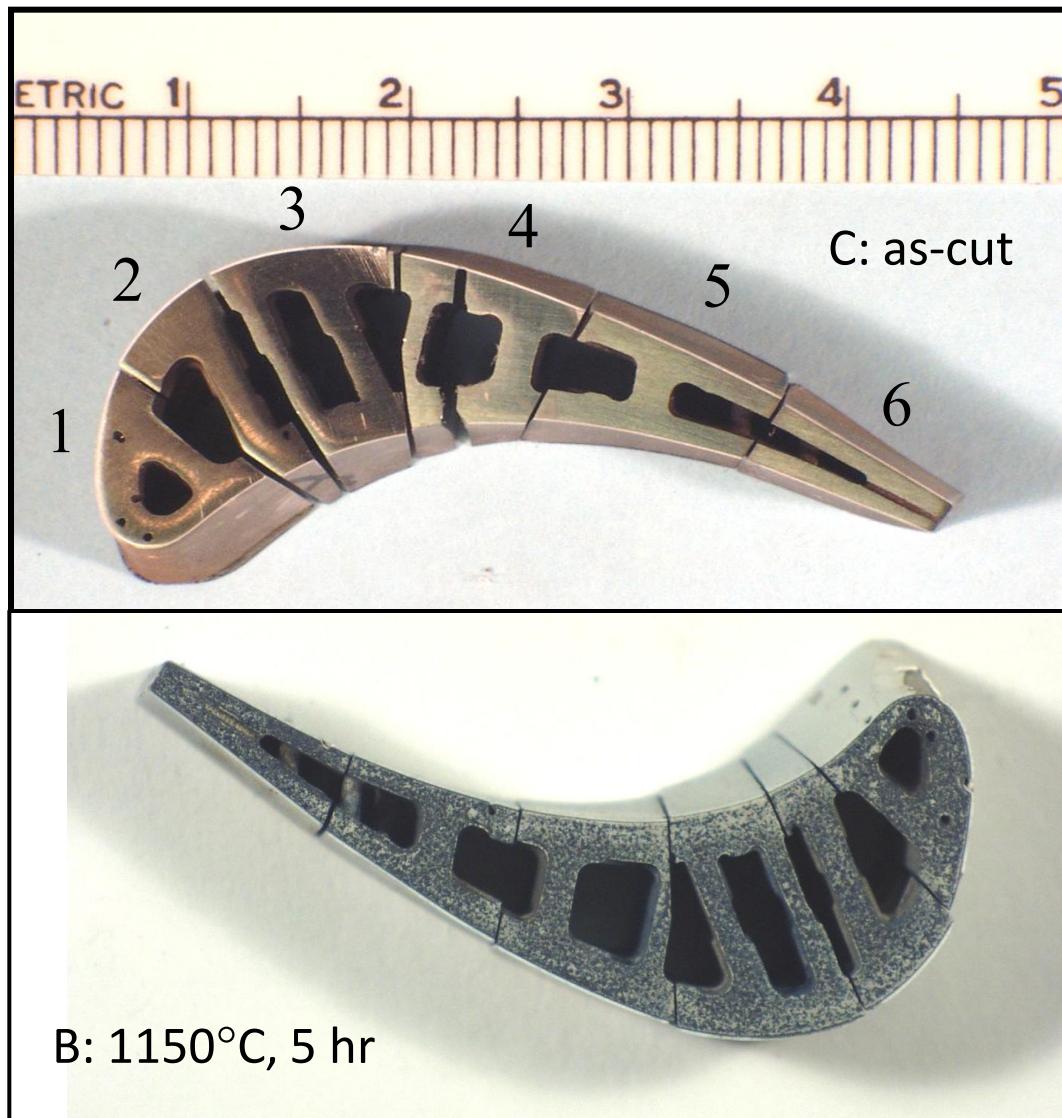


Figure 2

# Intermittent Oxidation of TBC on DS Turbine Blade

Blade Section A, 1100°C, 7YSZ on Ni(Pt)Al

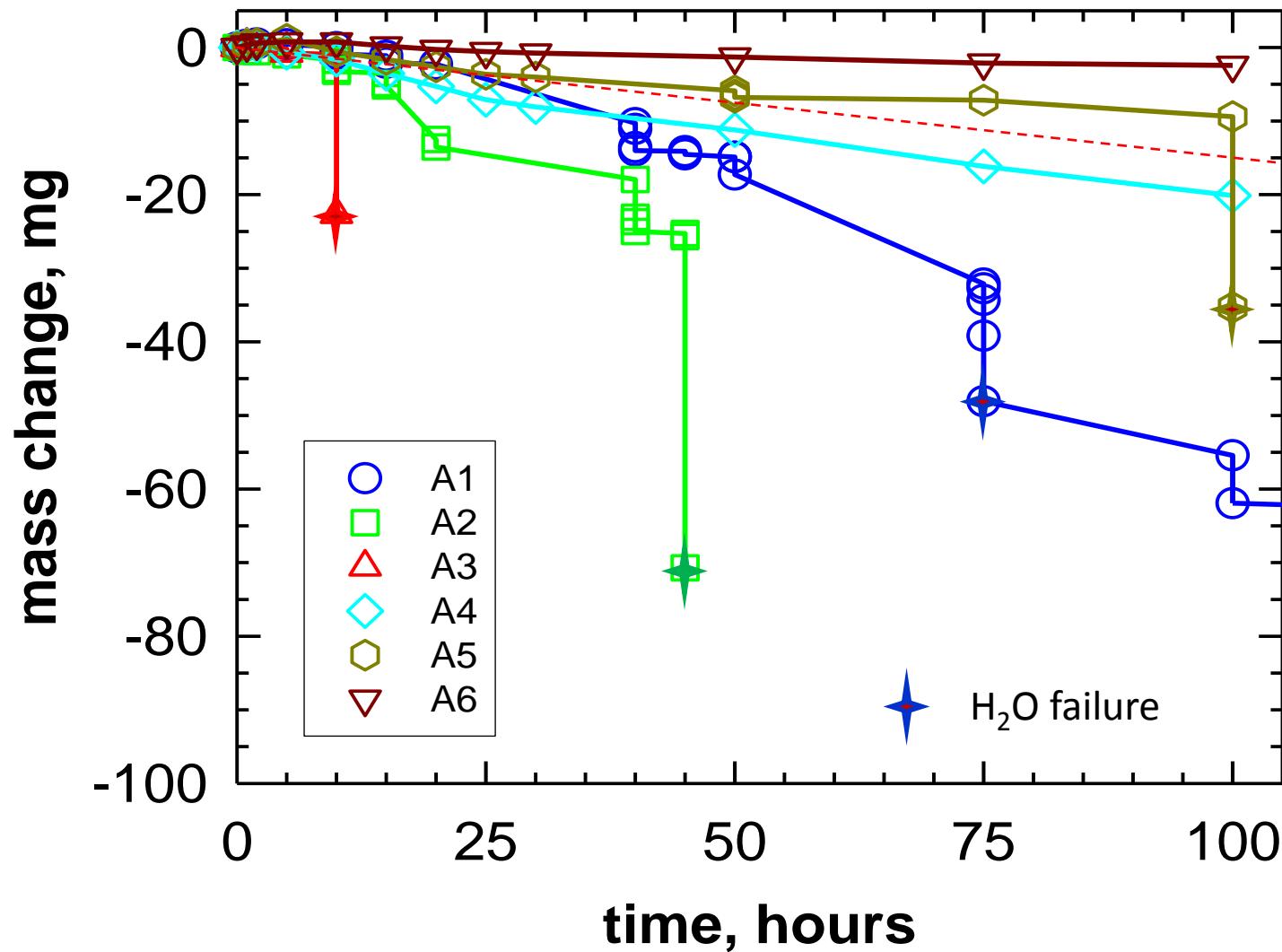


Figure 3

# TBC Oxidation Failure/Survival Times

Blade Section A; 1100°C

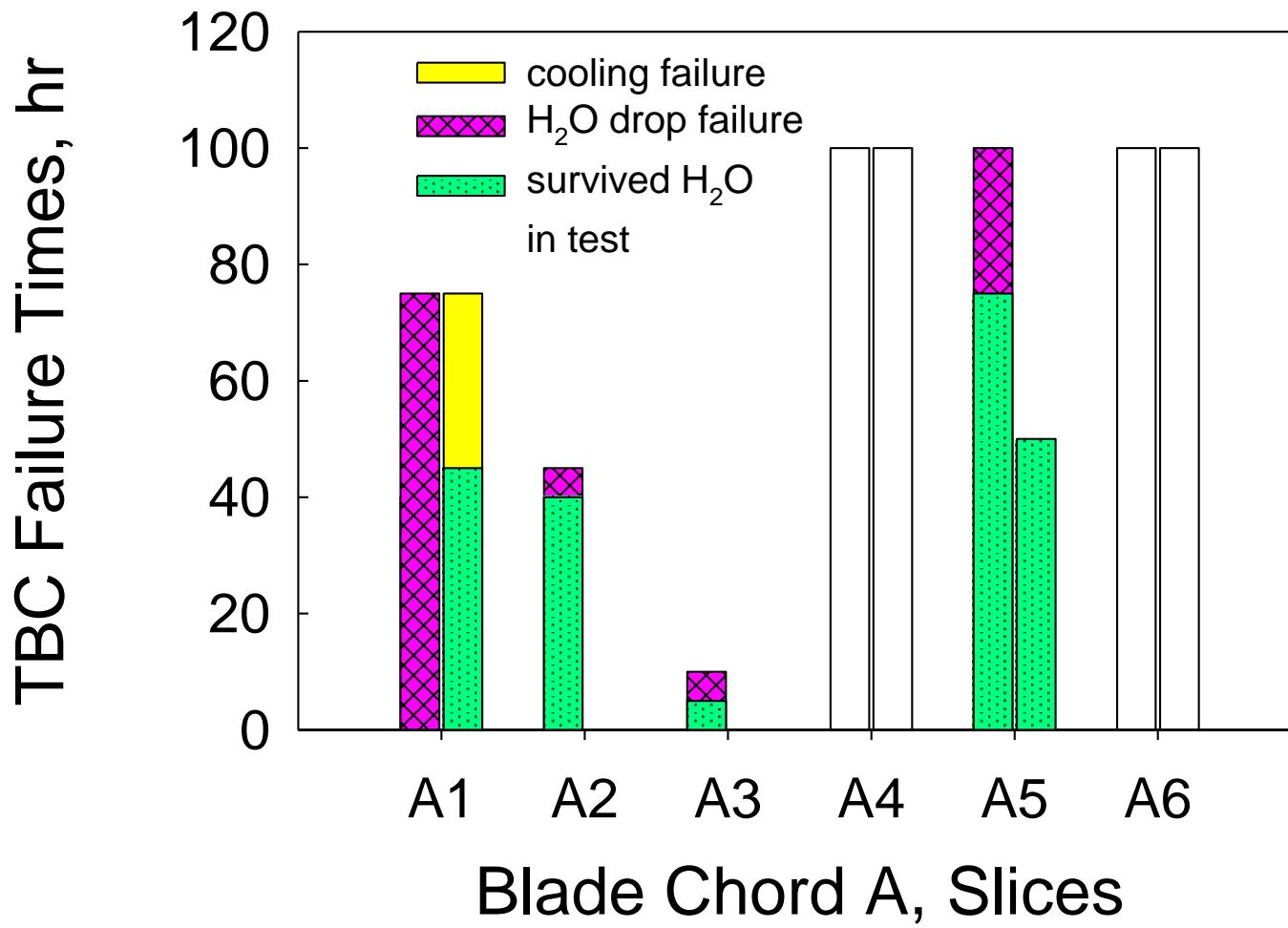


Figure 4

# Intermittent Oxidation of TBC on Turbine Blade

Blade Section B, 1150°C, 7YSZ on Ni(Pt)Al

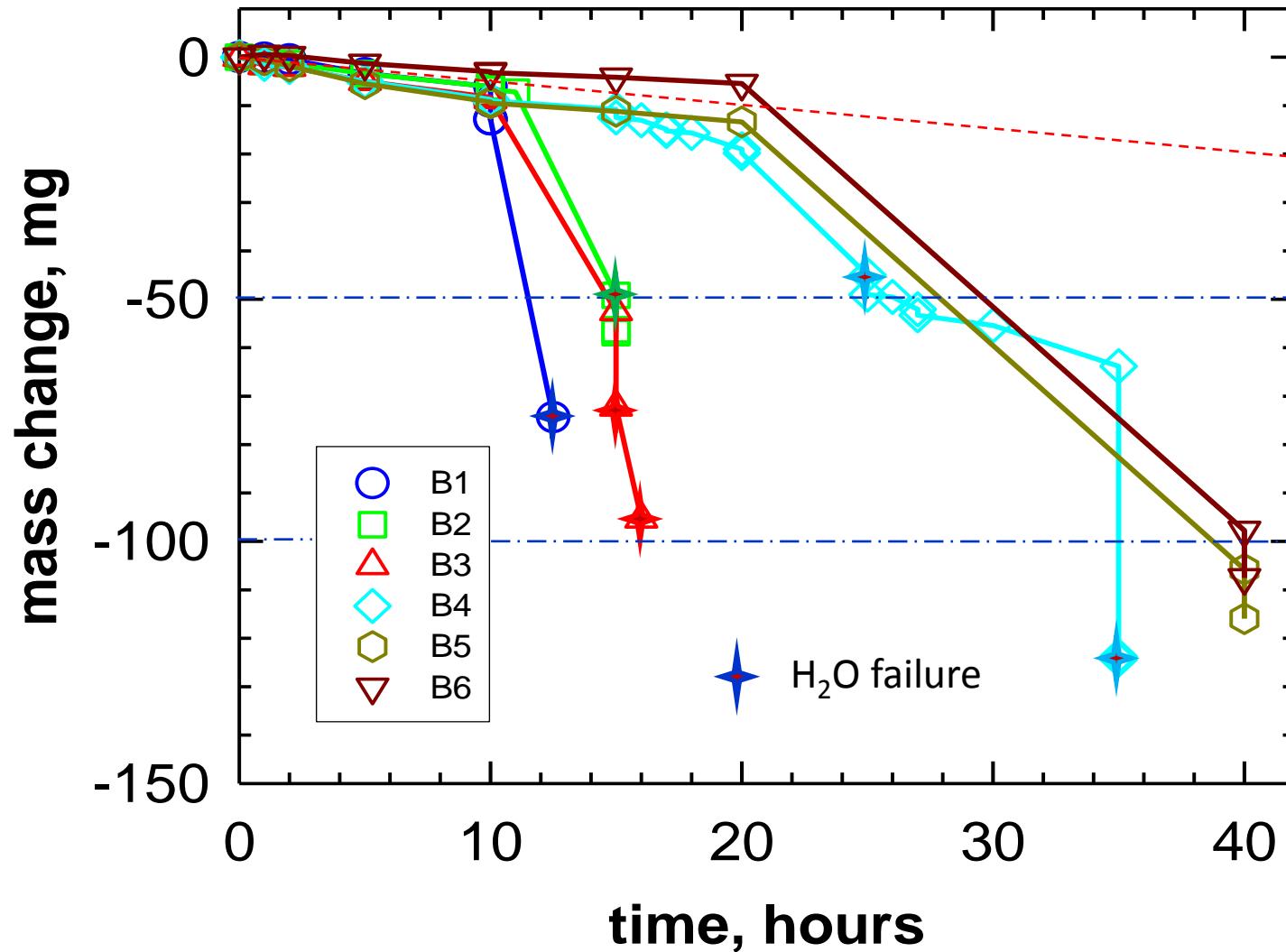


Figure 5

# TBC Oxidation Failure/Survival Times

Blade Section B; 1150°C

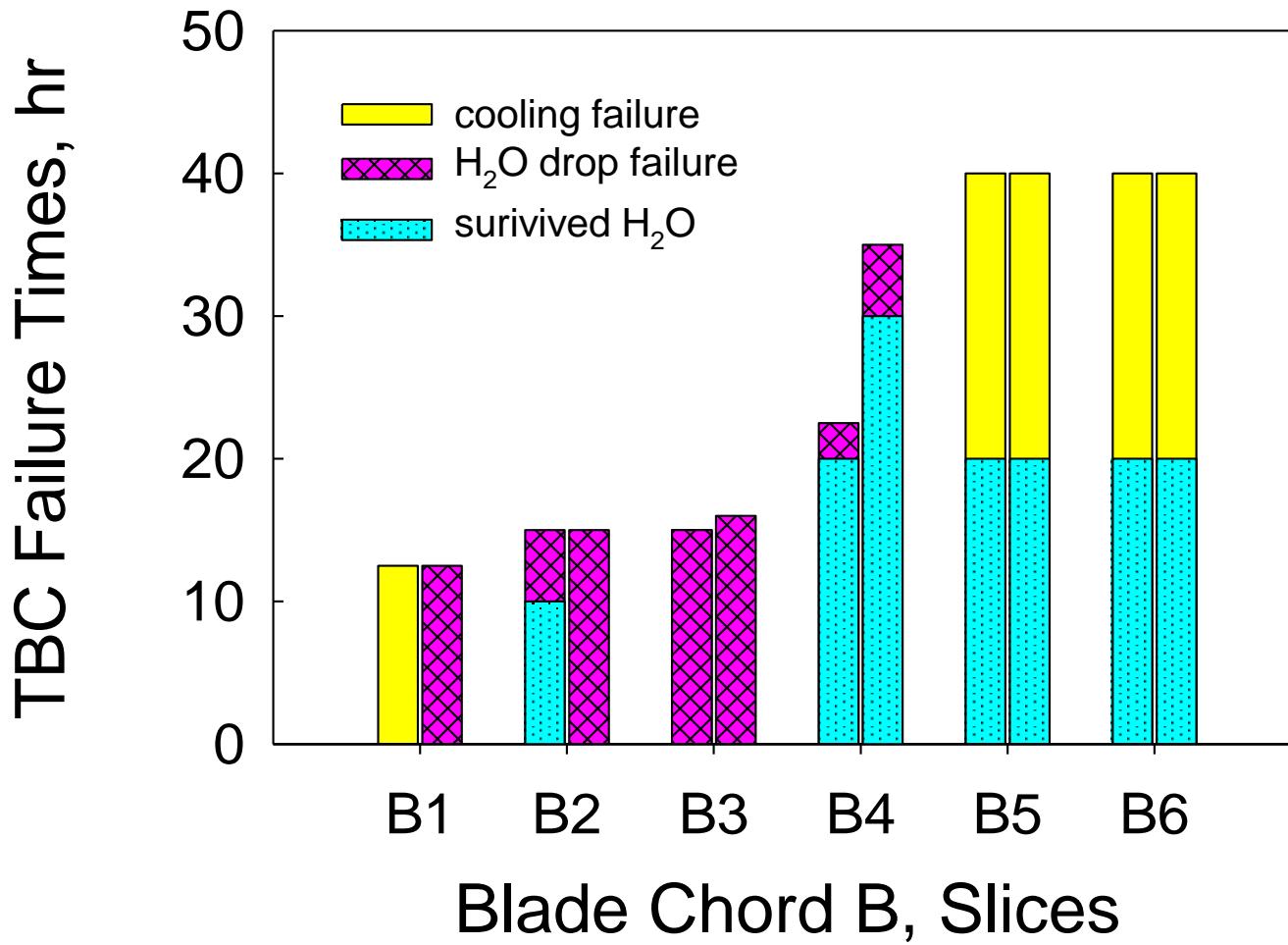


Figure 6

# Intermittent Oxidation of TBC on Turbine Blade

Blade Section C, 1200°C, 7YSZ on Ni(Pt)Al

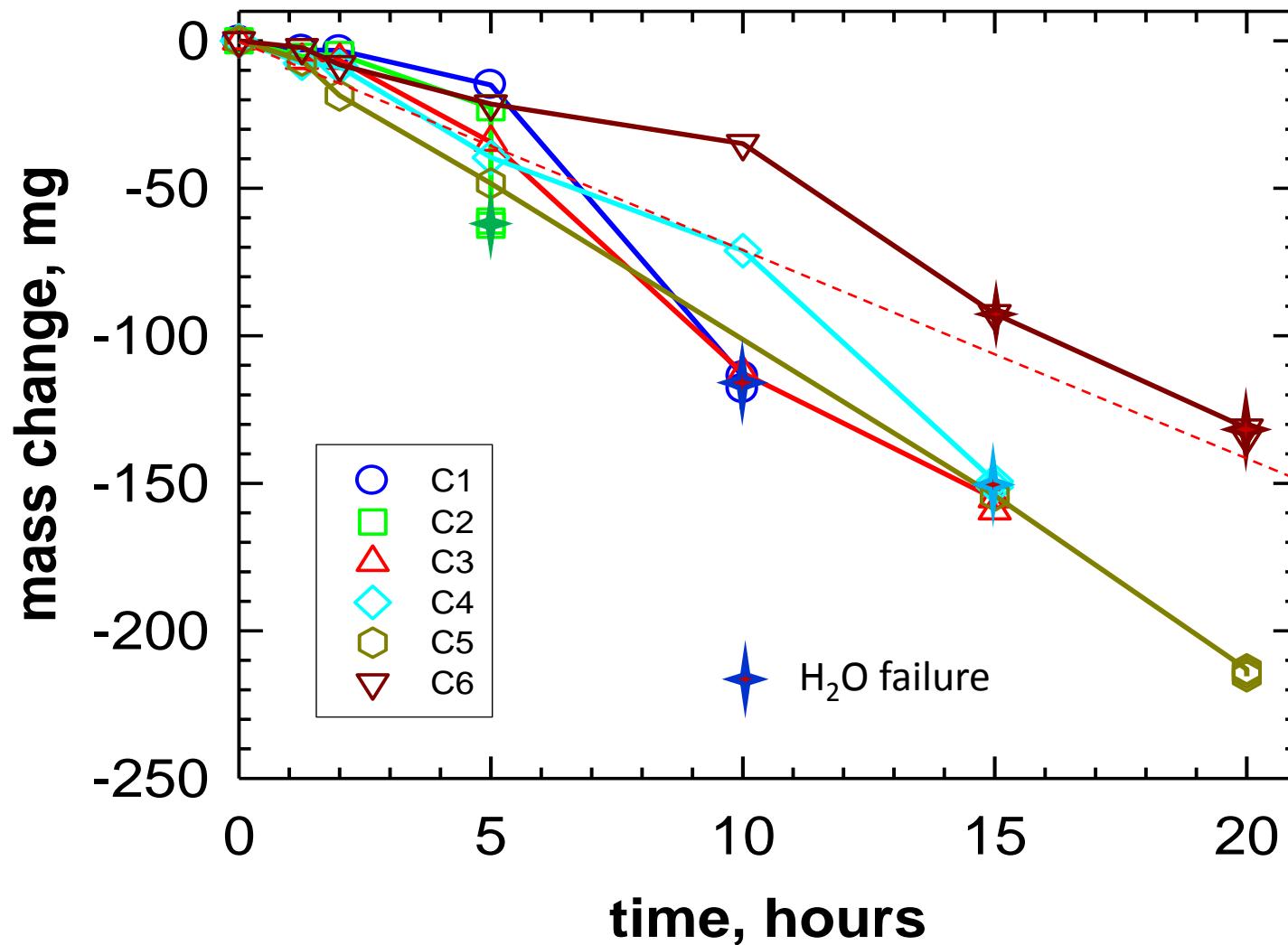


Figure 7

# TBC Oxidation Failure/Survival Times

Blade Section C; 1200°C

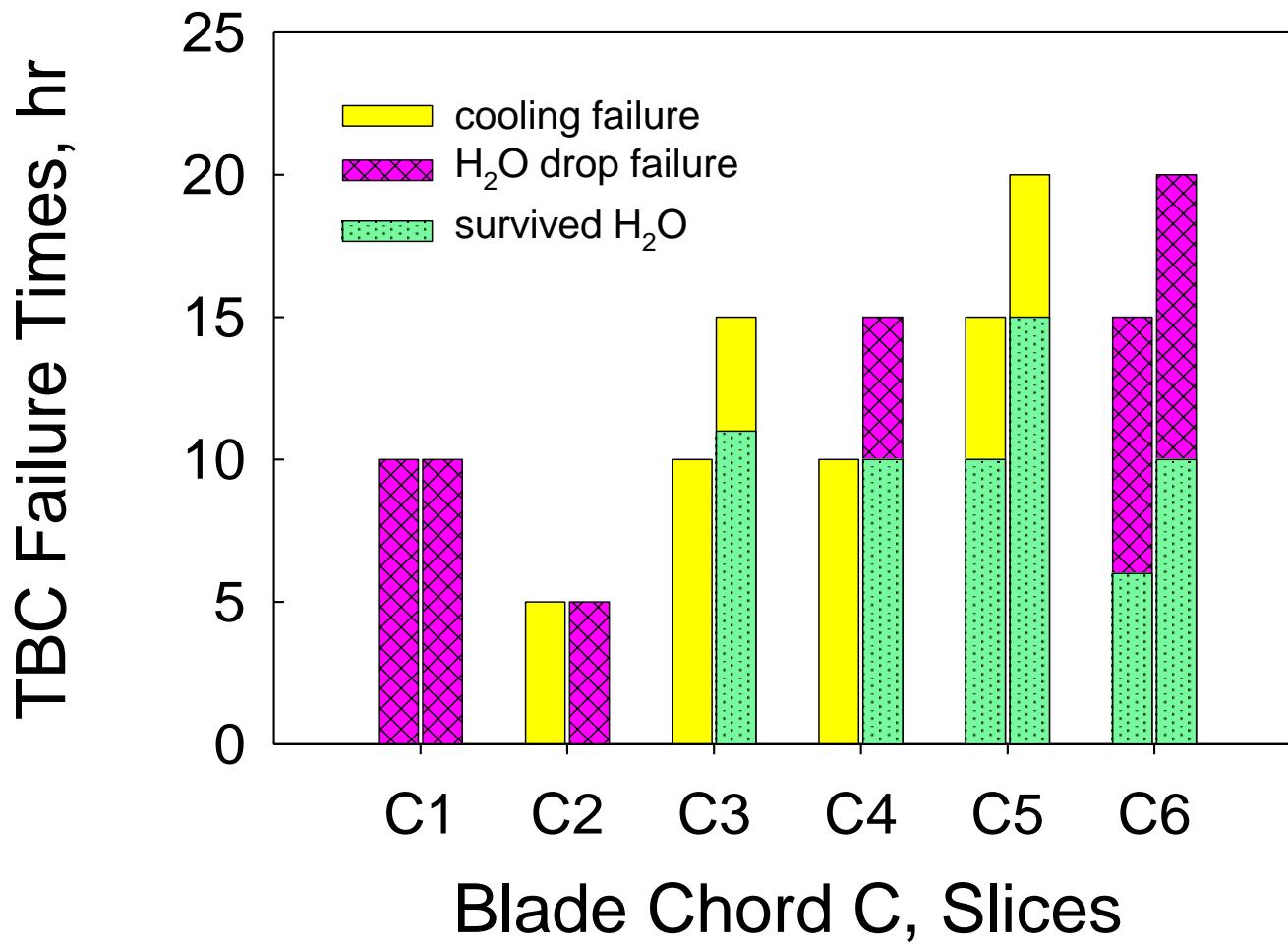


Figure 8

# Cut Section after Initial Oxidation

B2, 1150°C, 5 hr, 50x

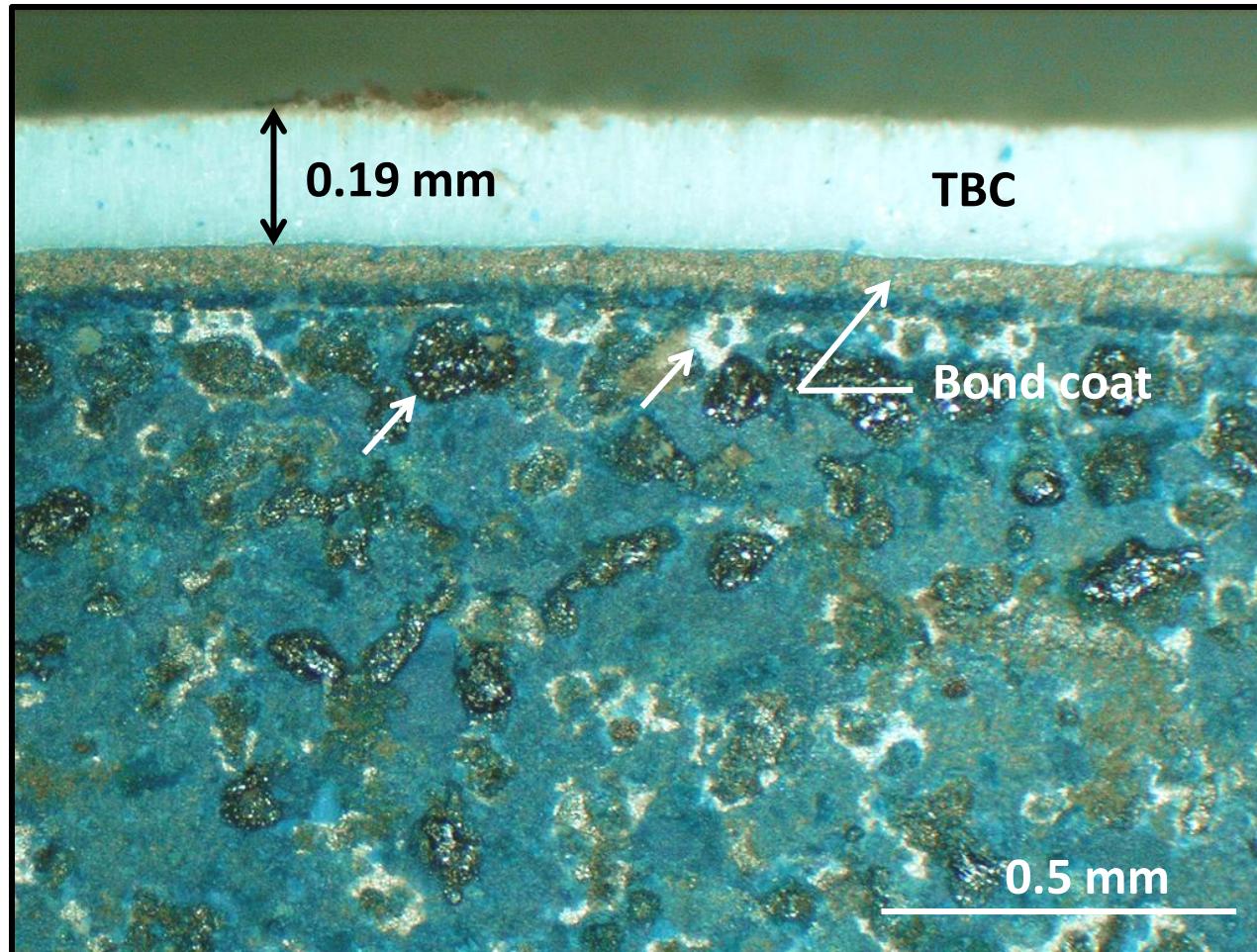
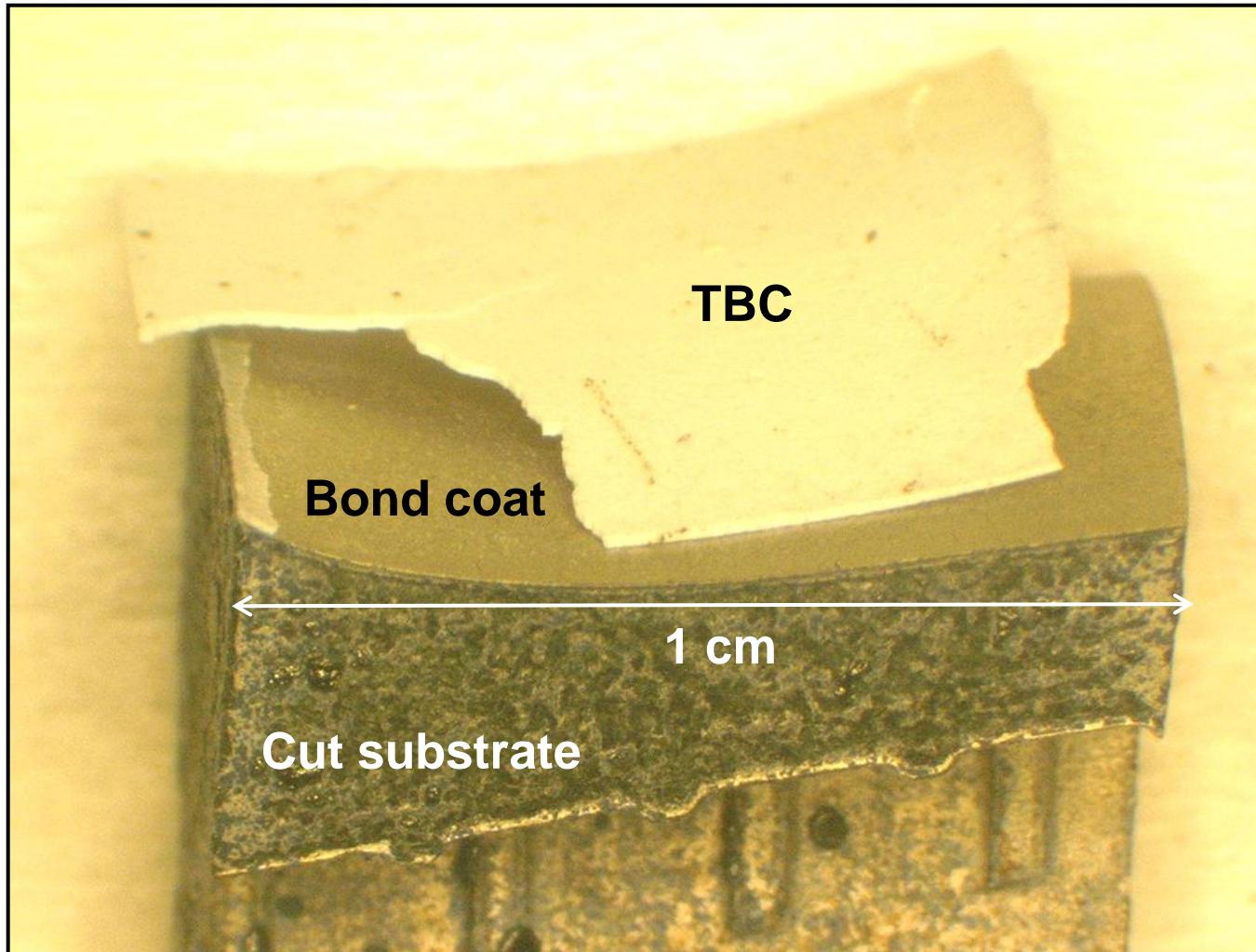


Figure 9

Sample C2: 1200°C, 5 hr.  
**100% Delamination after 2 min water immersion**



# Water Drop Spallation

A3, 1100°C, 10 hr, 10x

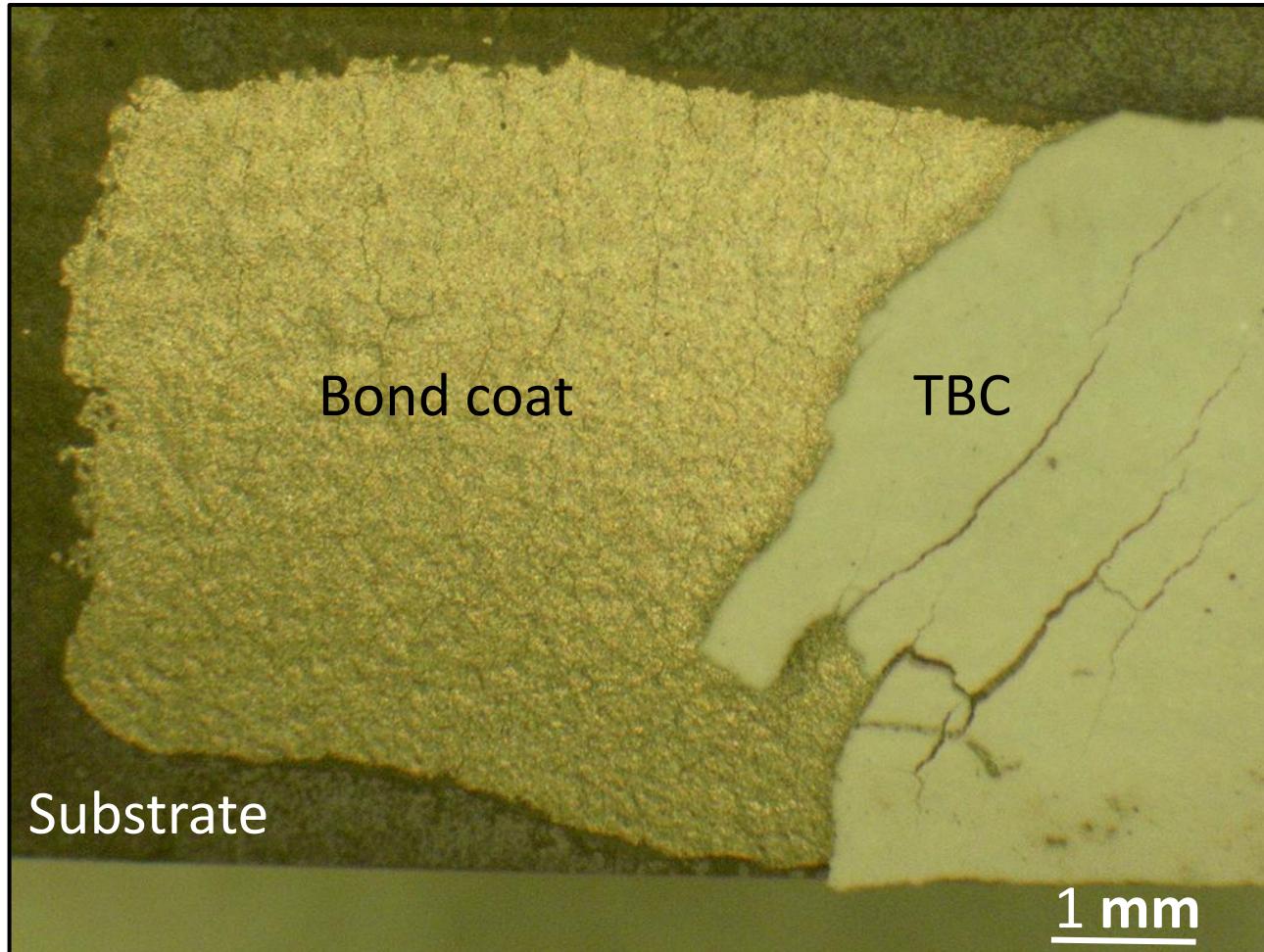
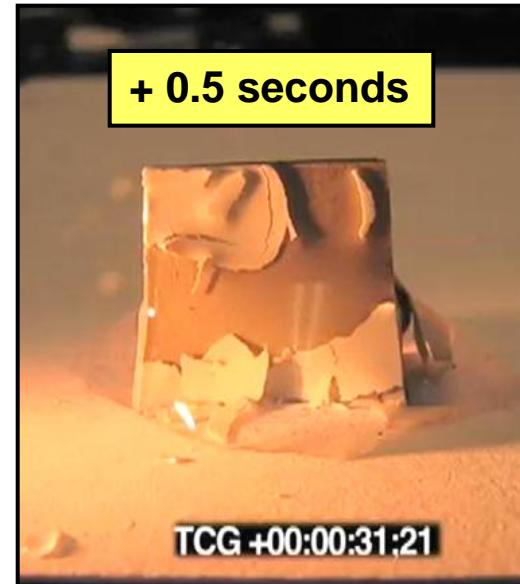
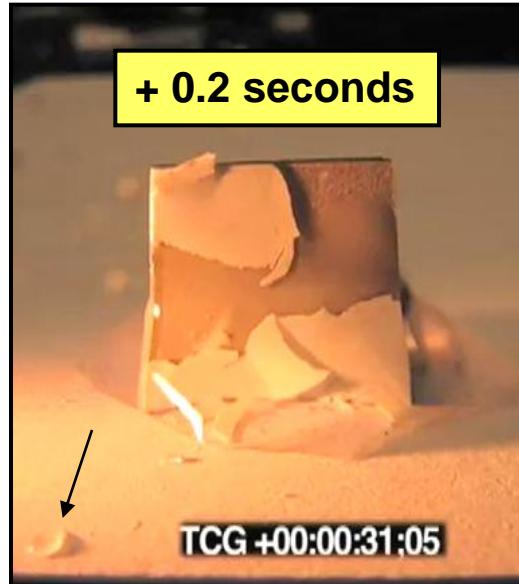
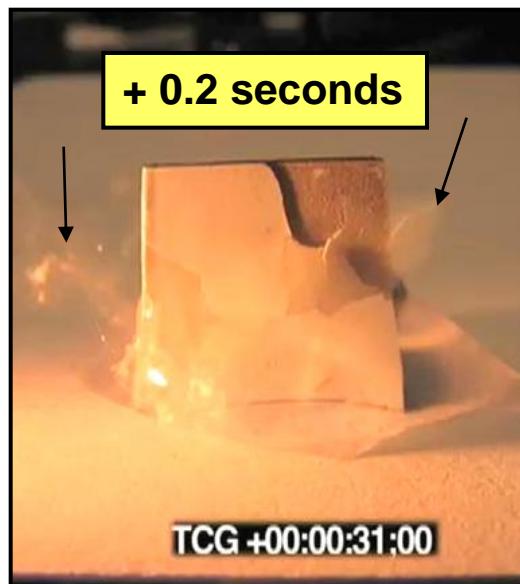
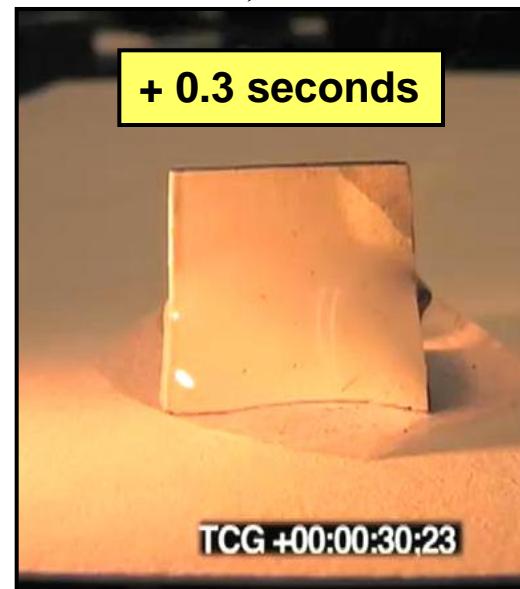
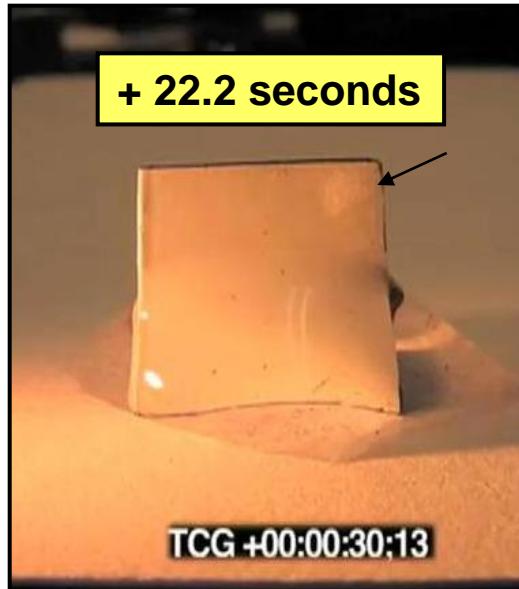
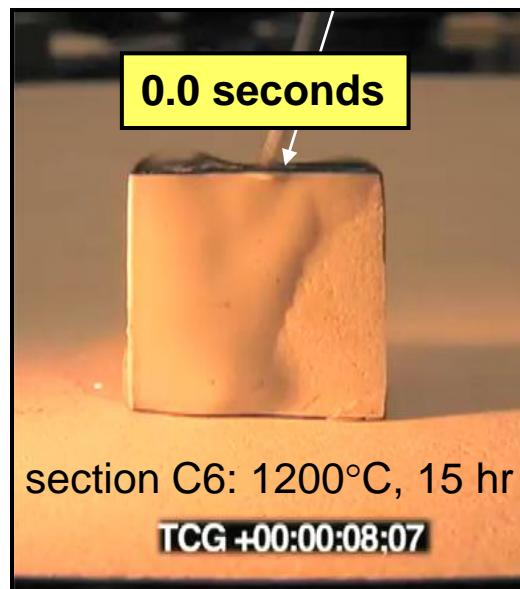


Figure 11

## Water Drop Failure Sequence of a TBC



# Metallic Interface Exposed by TGO/TBC Spallation

C2, 1200°C, 5 hr; 2 min. H<sub>2</sub>O failure; 100x



Figure 13

Spalled Oxide Underside: B4, 1150°, 35 hr  
**Scale Undulations and Grains**

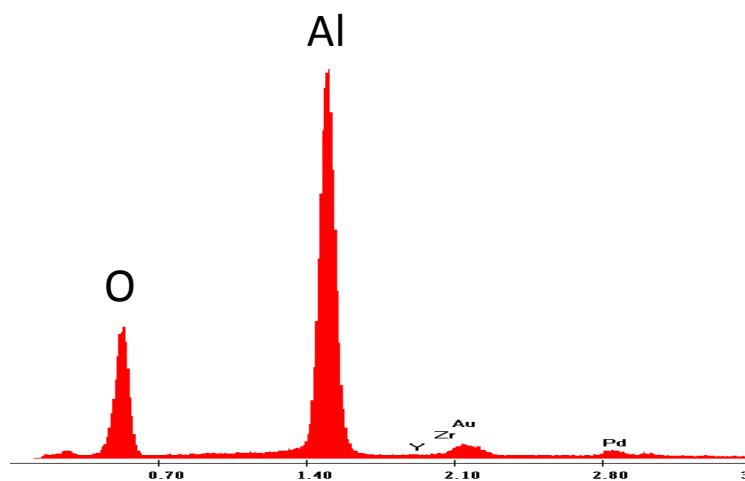
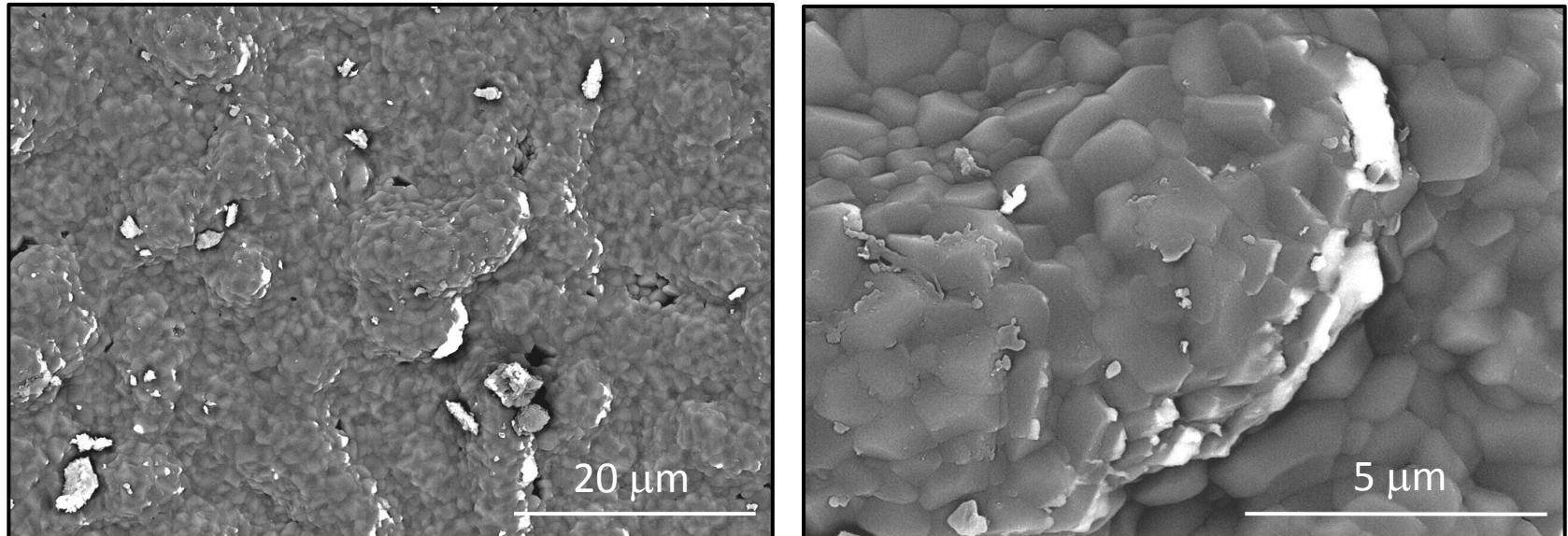


Figure 14

Spalled TBC Fracture Edge : B4, 1150°, 35 hr  
**Columnar EB-PVD YSZ Grains**

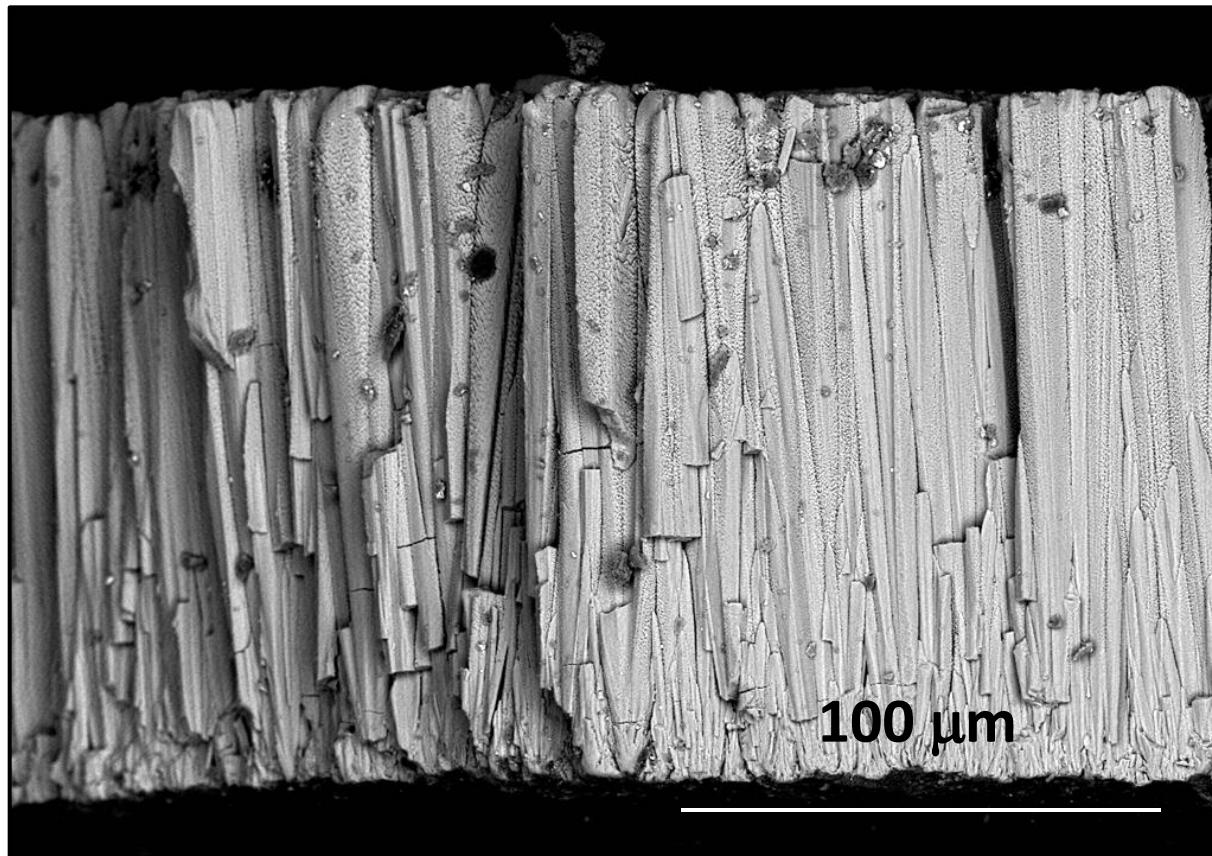


Figure 15

Exposed Bond Coat: B4, 1150°, 35 hr  
**Oxide Inclusion Network**

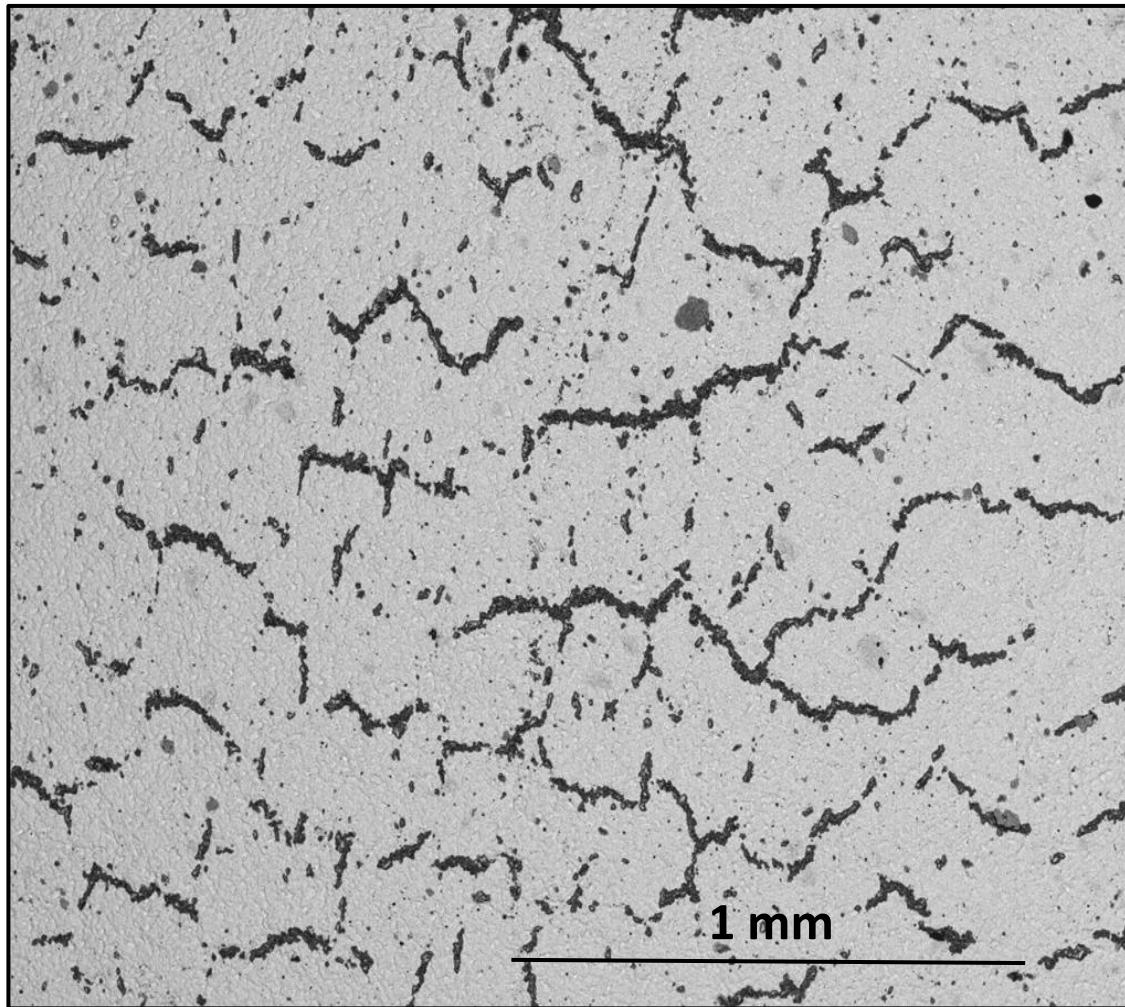


Figure 16

Exposed Bond Coat Surface: B4, 1150°, 35 hr  
 $\text{Al}_2\text{O}_3$  Stringer with Ta, Zr-Rich Oxide Inclusions

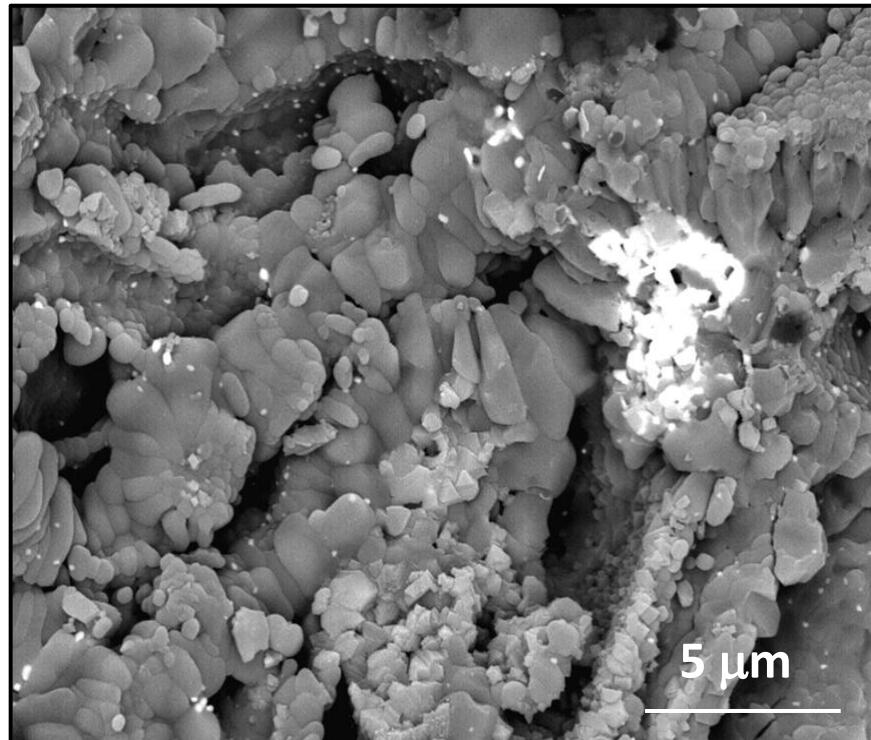
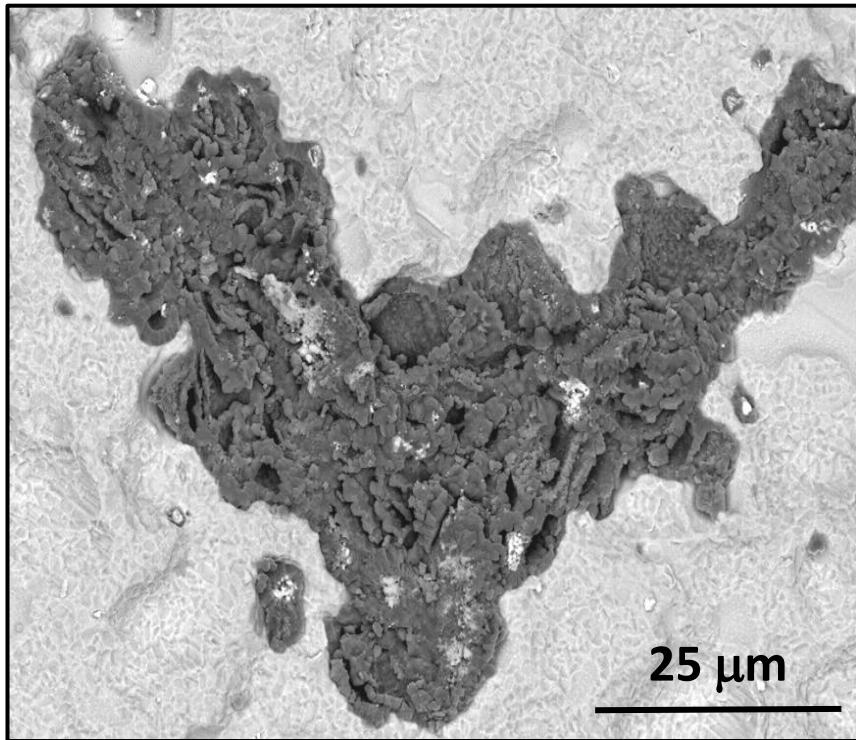


Figure 17

# Exposed Bond Coat Surface: B4, 1150°, 35 hr

## Oxide Grain Imprints in Metal

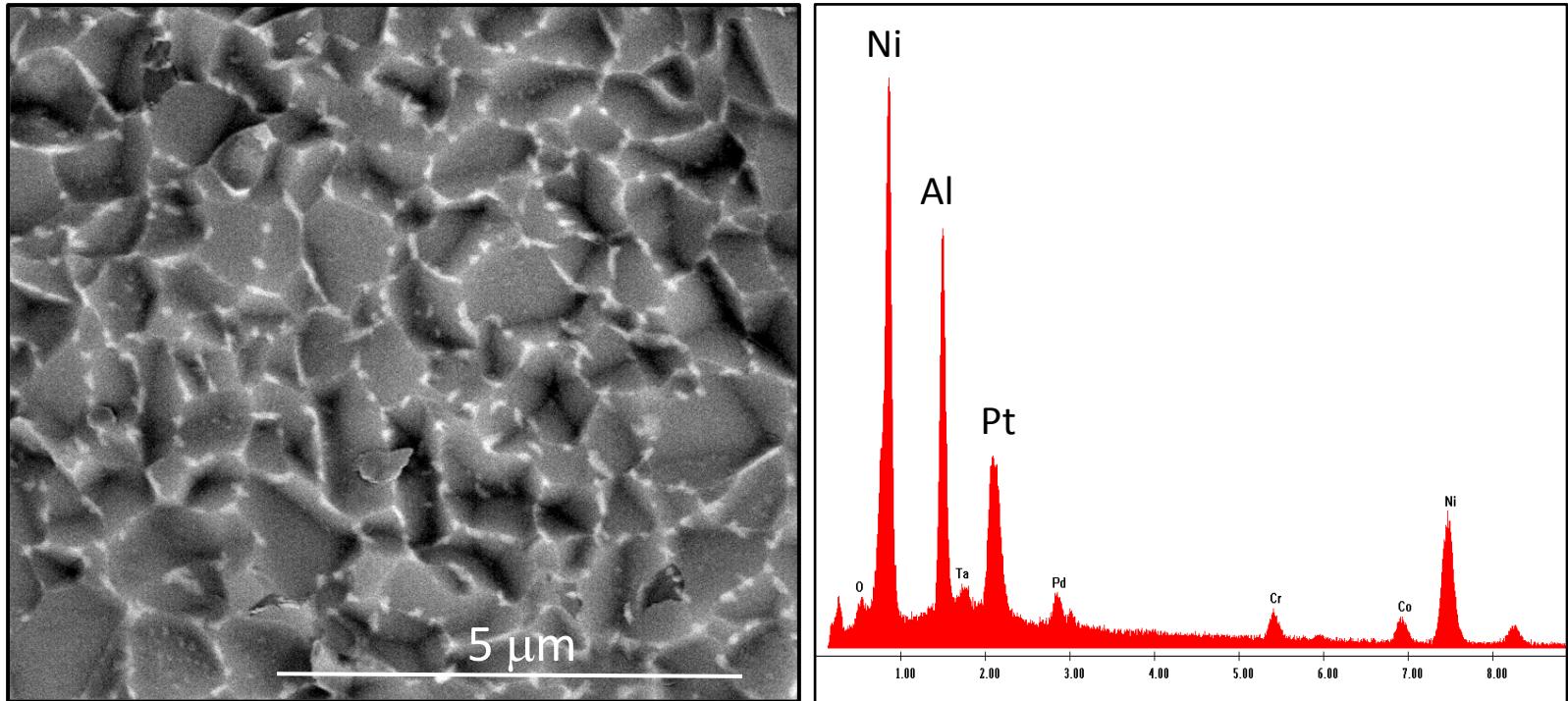


Figure 18